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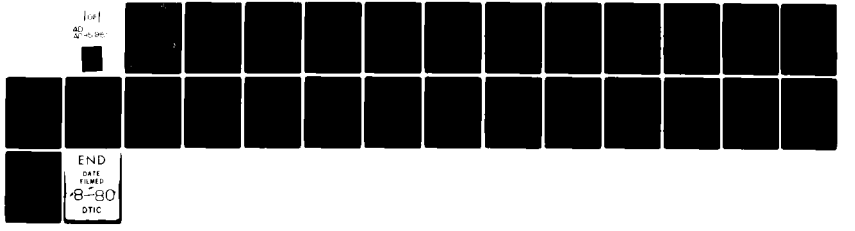

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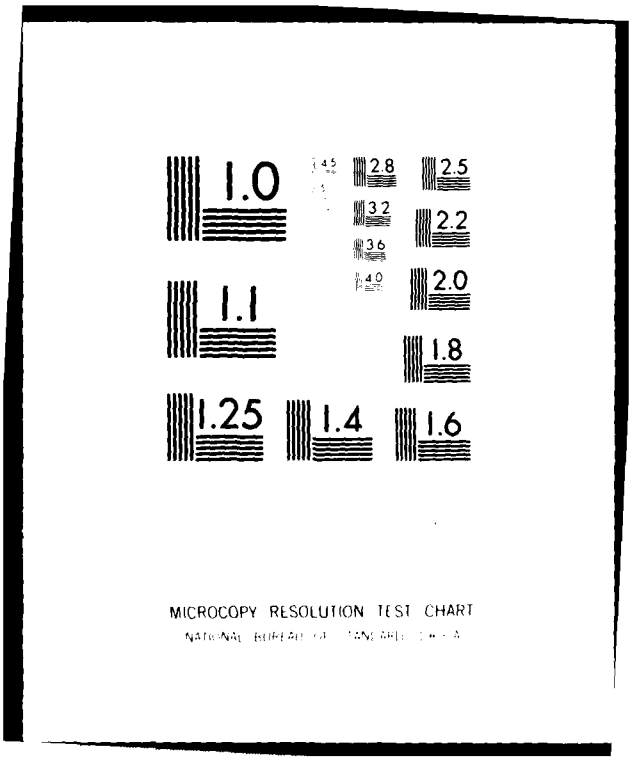
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of the eight Nd-N bond distances is 2.47(4) A. While one of the pthalocyanine macrocycles is slightly saucer-shaped towards the neodymium atom, the other is planar; anles of tile range from 2.5 to 7.0 . The neodymium atom is an equal distance of 1.47(1) A from each of the two macrcyclic planes. From EPR measurements, the title complex was found to contain an organic-free radical (g = 2.0029). Magnetic susceptibility measurements also demonstrated that the title complex contains one organic-free radical which could have an exchange interaction with f-electrons of the central neodymium(III) ion.

X-Ray Crystal Structure Analysis of Radical Bisphthalocyaninatoneodymium(III)

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Abstract: The molecular structure of bisphthalocyaninatoneodymium(III) has been determined by three-dimensional X-ray analysis. The orthorhombic cell dimensions and space group are a = 8.030(4), b = 22.925(7), and c = 28.315(7) A; Z = 4; V = 5212.4 (3.3 A); and $P2_12_12_1$. The final parameters were determined from 3505 independent reflections. The least-squares fitting of the data refined to R_1 = 7.4%. A neodymium ion occupies a central position between two parallel, but staggered (45°) phthalocyanine ligands. The average of the eight Nd-N bond distances is 2.47(4) A. While one of the phthalocyanine macrocycles is slightly saucer-shaped towards the neodymium atom, the other is planar; angles of tilt range from 2.5 to 7.0°. The neodymium atom is an equal distance of 1.47(1) A from each of the two macrocyclic planes. From EPR measurements, the title complex was found to contain an organic-free radical (g = 2.0029). Magnetic susceptibility measurements also demonstrated that the title complex contains one organic-free radical which could have an exchange interaction with f-electrons of the central neodymium(III) ion.

Introduction

Since the synthesis of copper(II) phthalocyanine was published as the first metallophthalocyanine in 1927,[2] many usual-type complexes of metallophthalocyanine have been reported.[3] Many studies have been done on semiconductivity, photoconductivity, photochemical reactivity, photosynthetic activity, luminescence, and fluorescence which are based on the highly conjugated system of metallophthalocyanines.[3] Bioinorganic interests have also centered on these compounds because metallophthalocyanines have much the same general structures as the naturally occurring metalloporphyrins.[4] Bisphthalocyaninatotin(IV) was the first complex of unusual geometry, and was synthesized by Barrett *et al.* in 1936.[5] Recently, the structure of this complex was elucidated by an X-ray diffraction analysis.[6] Though many kinds of metallophthalocyanines have been synthesized since the report of bisphthalocyaninatotin(IV), compounds having an unusual composition were not reported until sandwich-type complexes of f-elements were prepared.[7] Recently, intense attention has been also directed toward electrochromism of the bisphthalocyaninatolanthanide(III) complexes for color imaging and graphic displays.[8] We report here the results of the X-ray diffraction analysis, EPR, and magnetic susceptibility of the unusual type complex of bisphthalocyaninatoneodymium(III).

Experimental Section

1. Preparation of a Single Crystal. A purple single crystal (green in the powder) prepared by recrystallization of a blue bisphthalocyaninatoneodymium(III) complex from dichlorometahne was used for the X-ray analysis.

Anal. Calcd for $C_{64}H_{32}N_{16}Nd\cdot CH_2Cl_2$: Cl, 5.66%. Found: Cl, 5.71%. Mass. m/e 88 ($CH_2Cl_2^{37}$, 11%), 86 ($CH_2Cl^{37}Cl^{35}$, 67%) and 84 ($CH_2Cl_2^{35}$, 100%).[9] The synthesis of the blue bisphthalocyaninatoneodymium(III) complex has been described.[7(a),7(b)]

2. Physical Measurements. EPR spectra were obtained with a Varian E-3 spectrometer. Instrumental conditions: modulation = 0.63G; power = 5 mV; microwave frequency = 9.12 GHZ. The reported g-values were calculated using phosphorus doped silicon as standards. Magnetic susceptibility was measured with a Faraday method with mercury tetrathiocyanatocobaltate for calibration. Diamagnetic corrections were estimated from the diamagnetism of metal-free phthalocyanine, but were comparatively small.

3. X-ray Data. An opaque crystal of dimensions 0.10x0.28x0.55 mm was mounted on a fiber and used for the X-ray measurements. Cell constants and intensity data were obtained with an Enraf-Nonius CAD-4 diffractometer located at the Molecular Structure Corp. of College Station, Tx. MoK_α radiation (λ = 0.71073 Å) was obtained from a graphite crystal monochromator. Crystal and intensity data are presented in Table I. The data

Table I

were reduced using the following equations: $I = S(C-RB)$, $\sigma(I) = [S^2(C+R^2B) + 0.0025\ I^2]^{\frac{1}{2}}$, $|F_o| = (I/Lp)^{\frac{1}{2}}$, and $\sigma(F_o) = \sigma(I)/2|F_o|Lp$ (S is the scan rate, C is the total integrated peak count, B is the total background count, R is the ratio of scan time to background counting time and Lp is the Lorentz-polarization factor). On the basis of ψscans absorption corrections were omitted.

4. Solution and Refinement of the Structure. The structure was solved by the heavy atom method, and then refined by full-matrix least squares calculations using the crystallographic multipurpose SHELX program system (by George Sheldrick). Large correlation coefficients were noticed between the parameters of atoms related by a pseudo-mirror plane at y = 0.0000 (or 1.0000) on the initial cycles of least squares calculations. Also a molecule of crystallization, CH_2Cl_2 was discovered in a difference Fourier Map. The neodymium atom, nitrogen atoms N11, N31, N50, N70 and solvent atom C81 all have coordinates with y nearly equal to 1.0000. The parameters of these atoms did not have large correlation coefficients with other atomic parameters in the least squares calculations. Other space group possibilities were considered, but the systematic absences uniquely define it to be $P2_12_12_1$.

Continued refinement resulted in very unsatisfactory molecular geometry with large correlation coefficients for atomic parameters related by the pseudo-mirror at at y = 1.0000. The structure was then refined alternately in two segments; segment I: atoms N1-C15, C36-N40, N51-C69 and C11; segment II: atoms C16-C35, N41-C49, N71-N80 and C12 (Fig. 1). Parameters for the six atoms near the pseudo-mirror plane were common to both segments. This method greatly improved the bond distances and angles. Six of the phenyl rings were refined in such a way as to constrain the atomic positions to perfect hexagonal symmetry and carbon-carbon distances of 1.395 Å. The remaining two phenyl rings (in phthalocyanine I, the lower-numbered atoms) were not constrained since the pseudo-mirror plane bisects these rings. Hydrogen atoms (32) were included in the refinement with their positions altering with the positions of the

carbon atoms of the phenyl rings in such a way to maintain idealized geometry (C-H = 1.080 Å, C-C-H = 120°). An overall isotropic temperature factor for the hydrogen atoms refined to a final value of U = 0.055 $Å^2$. The neodymium and chlorine atoms were refined with individual anisotropic temperature factors. All other atoms had individual isotropic temperature factors. Positional parameters for the dichloromethane solvent were fixed at positions established from a difference Fourier map. The scattering factors and dispersion corrections for neodymium were taken from Vol. IV of the International Tables for X-ray Crystallography. The real and imaginery anomalons dispersion corrections for Nd were $\Delta f' = -0.535$ and $\Delta f'' = 3.018$, respectively. Scattering factors for C, H, N and Cl were incorporated in the SHELX system and taken from Acta Cryst.[10] The final agreement index R defined as $\frac{\Sigma||F_o|-|F_c||}{\Sigma|F_o|}$ is 0.074 and R_w defined as $\left(\frac{\Sigma w(|F_o|-|F_c|)^2}{\Sigma w F_o^2}\right)^{1/2}$ is 0.073. A final difference map had some peaks with y nearly equal to 1.000 and a maximum density of $0.8e \cdot Å^{-3}$. One other peak with y = 0.7774 of density $0.8e \cdot Å^{-3}$ was located 0.70 Å from C7 and 0.59 Å from H7. A table of observed and calculated structure factors is available as supplementary material.

Table 2

Results and Discussion

The Crystal Structure of Bisphthalocyaninatoneodymium(III). The structure of bisphthalocyaninatoneodymium can be represented by two phthalocyanine ring systems between which the neodymium atom occupies a central position (Fig. 1).

Figure 1

The phthalocyanine ligands are rotated 45° with respect to one another (Fig. 2).

Figure 2

The average of the eight Nd-N bond distances is 2.47(4) Å (Table 3).

Table 3

Angles in bisphthalocyaninatoneodymium(III) are listed in Table 4.

Table 4

While one of the phthalocyanine ligands is slightly saucer-shaped towards the neodymium atom, the other is planar; angles of tilt range from 2.5 to 7.0° (Table 5).

Table 5

The liganding nitrogen atoms deviate from the planes defined by the four nitrogen atoms bound to the metal atom by distances ranging from 0.04 to 0.18 Å (Table 5). The obviously tilted benzimidazole group is inclined 13° to the macrocyclic plane. Recently, X-ray diffraction analysis of bisphthalocyaninatouranium(IV) was also reported.[11] Comparison between bisphthalocyaninato-tin(IV), uranium(IV), and neodymium(III) is given in Table 6.

Table 6

The phenyl rings make angles of 2-14°, 6.6-17.1°, and 2.5-7.0° with

respect to the macrocyclic plane for tin(IV), uranium(IV), and neodymium(III) compounds, respectively.[6,11] Lux mentioned that the σ-bond of the uranium(IV) complex is stronger than that of the tin(IV) complex so that the SP^2-orbitals at the nitrogen atoms forming σ-bonds to the uranium atom are directed more strongly to the uranium atom.[12] The degree of shift from the staggered orientation of the uranium(IV) complex is larger than that of the tin(IV) complex because the phthalocyanine rings of the uranium(IV) complex are largely convexed so that the benzene rings of the two phthalocyanine ligands in the uranium(IV) complex need to be closer than those of the tin(IV) complex to make an effective interaction between them (the van der waals distance for an aromatic carbon atoms is 3.4 Å).[13] The neodymium(III) complex takes the staggered configuration because of little distortion of the phthalocyanine ligands.

EPR and Magnetic Susceptibility Results. From the EPR measurements, the green bisphthalocyaninatoneodymium(III) complex prepared by refluxing the blue complex in dichloromethane was found to contain an organic-free radical. In the EPR spectra of the blue and green species in the polycrystalline state, the latter exhibited a strong ERP signal (g = 2.0029), while the former did not show any EPR signal. The green compound diluted with the blue showed anisotropy (g_1 = 2.001, g_2 = 2.004) (Fig. 3).

Figure 3

No hyperfine structure of these signals was obtained in the solid (also in a dichloromethane solution) either at room temperature or at liquid nitrogen temperature, consistent with the case of a molecular complex of bisphthalocyaninatoeuropium(III) with iodine.[14] The spectrum is also the

same with that of the organic-free radical observed in the study of an electrochemical redox of lutetium phthalocyanine.[15] When the mixed solution of tetrahydrofuran and a small amount of dichloromethane containing the blue compound was irradiated by an ultraviolet light for several minutes, the color of the solution changed from blue to green, while it did not change in the dark (Fig. 4).[16]

Figure 4

An infrared study of the blue and green compounds showed that imine hydrogen of the phthalocyanine ligand of the blue compound is not present in the green.[17] These results suggest a photo-induced oxidation of the blue compound. That is, imine hydrogen of the blue compound is abstracted by a small amount of a photo-induced $CH_2C_1\cdot$ or $Cl\cdot$ radical as follows:

$$CH_2Cl_2 \xrightarrow{h\nu} CH_2Cl\cdot + Cl\cdot \qquad (1)$$

$$\text{blue - } Pc_2NdH + CH_2Cl\cdot \text{ (or } Cl\cdot) \rightarrow$$
$$\text{green - } PcNd\dot{P}c + CH_3Cl \text{ (or HCl)} \qquad (2)$$

where Pc represents phthalocyanine dianion. Initially, a σ-radical may be generated and subsequently turns to a stable π-radical. Magnetic susceptibility measurements of these compounds demonstrated that the blue complex has three unpaired electrons, while the green has four unpaired electrons (Table 7).

Table 7

The magnetic susceptibility of the green complex showed a magnetic field

dependence, while that of the blue was not dependent on the magnetic field. Furthermore, the effective magnetic moment of the green complex decreased with decreasing temperature, but that of the blue did not change significantly with decreasing temperature (Table 7). These magnetic results demonstrate that the green complex contains one organic-free radical, which could have an exchange interaction with the f-electrons of the central neodymium(IV) ion, as is found in some radicals of 3d-transition metal complexes of phthalocyanine.[18]

ACKNOWLEDGEMENTS

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9. The mass spectrum was measured in the temperature of 300-340°C to identify existence of dichloromethane in the compound. At this temperature, bisphthalocyaninatoneodymium(III)did not sublime.

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16. The mixed solution of the blue compound in a test tube cooled by water was irradiated by UV. After irradiating over 30 minutes, the compound was decomposed and a small amount of purple precipitate was obtained.

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TABLE I. Crystal Data

Formula: $C_{64}H_{32}N$ Nd·CH_2Cl_2	Reflections measured: 4736
F.Wt.: 1254.1>	Significant Reflections ($F_o > 35_F$): 3505
Space group: $P2_12_12_1$	Scan Range (θ): 0.6-0.76°
Cell constents: a=8.030(4) Å	Scan Rate: 2-20°/min.
b=22.925(7)	(2θ) max: 50°
c=28.315(7)	Mokα radiation: 0.71073Å
V=5212.4(3.3)Å^3	
Z=4 for = 1.598 g·cm	
Crystal size = 0.10X0.28X0.55mm	
u=11.71 cm^{-1}	

TABLE 2. Fractional coordinates ($\times 10^4$) and thermal parameters ($\times 10^4$)

	X	Y	Z	U11*	U22	U33	U12	U13	U23
Nd	-1155(1)	1002(1)	3854(0)	292(3)	247(3)	245(3)	44(8)	- 5(3)	13(7)
C11	1913	- 629	1619	1952(107)	1601(86)	1561(85)	-345(83)	102(78)	-311(70)
C12	1924	633	1638	1004(49)	920(44)	857(44)	123(37)	26(34)	142(37)
C81	2419	- 11	1963	1258(80)					

	X	Y	Z	U		X	Y	Z	U
N1	402(15)	9187(5)	3567(4)	295(27)	N41	3693(13)	9341(4)	3754(4)	229(25)
C2	- 274(17)	8778(6)	3241(5)	266(30)	C42	3645(24)	8797(8)	3891(6)	554(48)
C3	- 71(14)	8187(3)	3319(4)	414(38)	C43	-4507(12)	8486(4)	3497(3)	438(39)
C4	- 454(14)	7660(3)	3099(4)	443(39)	C44	-4725(12)	7898(4)	3388(3)	212(27)
C5	86(14)	7135(3)	3295(4)	485(41)	C45	-5689(12)	7737(4)	3000(3)	434(39)
C6	1010(14)	7137(3)	3712(4)	413(37)	C46	-6434(12)	8164(4)	2720(3)	502(42)
C7	1394(14)	7664(3)	3933(4)	670(56)	C47	-6216(12)	8752(4)	2829(3)	390(35)
C8	854(14)	8189(3)	3736(4)	497(44)	C48	-5252(12)	8914(4)	3217(3)	487(42)
C9	1341(28)	8815(10)	3875(7)	784(62)	C49	-4689(14)	9472(5)	3387(4)	129(23)
N10	2223(13)	8954(4)	4229(4)	246(25)	N50	-5177(12)	9996(11)	3199(3)	360(22)
N11	1743(12)	10057(8)	4131(3)	344(27)	N51	-3639(16)	10610(6)	3747(5)	459(33)
C12	2551(15)	9576(5)	4330(4)	183(26)	C52	-4661(24)	10498(8)	3378(6)	535(46)
C13	3566(20)	9688(7)	4725(6)	433(38)	C53	-5283(11)	11041(3)	3188(3)	219(27)
C14	4403(26)	9344(10)	5022(8)	691(57)	C54	-6272(11)	11175(3)	2798(3)	436(38)
C15	5228(22)	9622(7)	5383(6)	490(43)	C55	-6645(11)	11756(3)	2694(3)	445(41)
C16	5413(22)	10198(7)	5381(6)	509(45)	C56	-6028(11)	12201(3)	2980(3)	332(33)
C17	4536(20)	10616(7)	5071(6)	432(39)	C57	-5039(11)	12067(3)	3370(3)	546(45)
C18	3607(22)	10277(8)	4707(6)	532(44)	C58	-4666(11)	11487(3)	3474(3)	177(26)
C19	2331(19)	10552(6)	4343(5)	355(35)	C59	-3580(12)	11205(4)	3811(4)	89(21)
N20	2062(19)	11038(6)	4236(5)	535(38)	N60	-2892(12)	11461(4)	4194(3)	176(23)
N21	305(13)	10917(4)	3563(4)	222(23)	N61	-1743(14)	10599(5)	4558(4)	293(27)
C22	1153(12)	11219(4)	3866(4)	76(20)	C62	-1839(19)	11182(6)	4514(5)	381(35)
C23	1011(12)	11817(3)	3751(3)	241(29)	C63	-1035(11)	11477(4)	4921(3)	322(32)
C24	1454(12)	12342(3)	3966(3)	448(40)	C64	- 735(11)	12058(4)	5041(3)	370(38)
C25	924(12)	12870(3)	3773(3)	835(67)	C65	254(11)	12191(4)	5432(3)	412(37)
C26	- 50(12)	12873(3)	3365(3)	801(66)	C66	942(11)	11743(4)	5702(3)	318(32)
C27	- 494(12)	12347(3)	3150(3)	580(48)	C67	642(11)	11162(4)	5582(3)	261(30)
C28	36(12)	11819(3)	3343(3)	407(39)	C68	- 347(11)	11029(4)	5192(3)	435(40)
C29	- 446(21)	11205(7)	3205(6)	422(39)	C69	- 786(23)	10482(8)	4955(7)	576(47)
N30	-1171(14)	11040(5)	2839(4)	250(23)	N70	- 300(12)	10004(11)	5138(3)	346(21)
N31	-1032(11)	9979(9)	2986(3)	323(22)	N71	-1574(14)	9380(5)	4547(4)	263(26)
C32	-1438(15)	10462(5)	2724(4)	220(27)	C72	- 758(13)	9469(5)	4954(4)	127(24)
C33	-2089(19)	10220(6)	2260(5)	369(38)	C73	- 371(12)	8903(3)	5153(3)	294(31)
C34	-2680(20)	10527(7)	1863(6)	425(39)	C74	708(12)	8729(3)	5512(3)	516(45)
C35	-3094(21)	10217(6)	1466(6)	446(41)	C75	959(12)	8137(3)	5601(3)	442(40)
C36	-3365(18)	9615(6)	1519(5)	338(35)	C76	131(12)	7719(3)	5331(3)	376(36)
C37	-2669(18)	9298(7)	1895(5)	359(34)	C77	- 948(12)	7893(3)	4972(3)	328(33)
C38	-2126(16)	9632(5)	2273(4)	231(29)	C78	-1200(12)	8485(3)	4883(3)	385(35)
C39	-1353(22)	9486(8)	2717(6)	492(43)	C79	-1980(15)	8783(5)	4509(4)	195(27)
N40	-1107(17)	8943(6)	2833(5)	467(33)	N80	-2690(18)	8506(6)	4174(5)	493(37)

*The anisotropic thermal parameters U_{ij} are the mean-square amplitudes of vibration in $Å^2$. They are introduced into the structure factor expression as $T=\exp[-2\pi^2(U_{11}h^2a^{*2}+U_{22}k^2b^{*2}+U_{33}l^2c^{*2}+2U_{12}a^*b^*hk+2U_{13}a^*c^*hl+2U_{23}b^*c^*kl)]$.

TABLE 3. Interatomic Distances for Neodymium Phthalocyanine.

Neodymium - Nitrogen

Phthalocyanine I		Phthalocyanine II	
N1	2.390(11) Å	N41	2.490(11)
N11	2.459(10)	N51	2.453(13)
N21	2.542(10)	N61	2.463(11)
N31	2.461(9)	N71	2.446(11)

Phthalocyanine I

$N_{pyrrole}$ - C

N1-C2	1.43(2) Å
N1-C9	1.43(3)
N11-C12	1.39(2)
N11-C19	1.37(2)
N21-C22	1.30(1)
N21-C29	1.35(2)
N31-C32	1.37(2)
N31-C39	1.39(3)

$C_{pyrrole}$ - $C_{pyrrole}$

C2-C3	1.38(1) Å
C3-C8	1.39(1)
C8-C9	1.54(3)
C12-C13	1.41(2)
C13-C18	1.35(2)
C18-C19	1.58(2)
C22-C23	1.41(1)
C23-C28	1.39(1)
C28-C29	1.51(2)
C32-C33	1.52(2)
C33-C38	1.35(2)
C38-C39	1.44(2)

N_{bridge} - $C_{pyrrole}$

N10-C9	1.27(2)
N50-C49	1.37(2)
N50-C52	1.32(3)
N60-C59	1.35(1)
N60-C62	1.39(2)
N10-C12	1.48(2)
N20-C19	1.18(2)
N20-C22	1.34(2)
N30-C29	1.25(2)
N30-C32	1.38(2)
N40-C39	1.30(2)
N40-C2	1.39(2)
N70-C69	1.27(3)
N70-C72	1.38(3)
N80-C79	1.28(2)
N80-C42	1.29(2)

Phenyl rings

C13-C14	1.34(3)
C14-C15	1.38(3)
C15-C16	1.33(2)
C16-C17	1.48(2)
C17-C18	1.49(2)
C18-C13	1.35(2)
C33-C34	1.41(2)
C34-C35	1.37(2)
C35-C36	1.40(2)
C36-C37	1.40(2)
C37-C38	1.39(2)
C38-C33	1.35(2)

Solvent Molecule, CH_2Cl_2

Cl1-C81	1.77
Cl2-C81	1.79
Cl1-C81-Cl2	109°

Phthalocyanine II

$N_{pyrrole}$ - C		$C_{pyrrole}$ - $C_{pyrrole}$	
N41-C42	1.42(2)	C42-C43	1.49(2)
N41-C49	1.32(1)	C48-C49	1.44(1)
N51-C52	1.35(2)	C52-C53	1.44(2)
N51-C59	1.38(2)	C58-C59	1.44(1)
N61-C62	1.35(2)	C62-C63	1.48(2)
N61-C69	1.39(2)	C68-C69	1.47(2)
N71-C72	1.34(2)	C72-C73	1.45(1)

N_{bridge} - $C_{pyrrole}$			
N50-C49	1.37(2)	N70-C69	1.27(3)
N50-C52	1.32(3)	N70-C72	1.38(3)
N60-C59	1.35(1)	N80-C79	1.28(2)
N60-C62	1.39(2)	N80-C42	1.29(2)

TABLE 4. Valency angles for Neodymium Phthalocyanine

Phthalocyanine I

N1-Nd-N11	69.7(5)°	N1-C2-C3	120(1)°
N1-Nd-N31	67.8(5)	N1-C2-N40	123(1)
N11-Nd-N21	68.0(5)	C3-C2-N40	118(1)
N21-Nd-N31	71.0(5)	C2-C3-C4	139(1)
Nd-N1-C2	122(1)	C2-C3-C8	101(1)
Nd-N1-C9	122(1)	C3-C8-C9	111(1)
C2-N1-C9	102(1)	C7-C8-C9	129(1)
Nd-N11-C12	122(1)	N1-C9-C8	105(2)
Nd-N11-C19	121(1)	N1-C9-N10	129(2)
C12-N11-C19	109(1)	C8-C9-N10	126(2)
Nd-N21-C22	118(1)	N10-C12-N11	127(1)
Nd-N21-C29	116(1)	N10-C12-C13	116(1)
N22-N21-C29	118(1)	N11-C12-C13	117(1)
Nd-N31-C32	121(1)	C12-C13-C14	133(2)
Nd-N31-C39	124(1)	C12-C13-C18	99(1)
C32-N31-C39	109(1)	C14-C13-C18	127(2)
C9-N10-C12	120(1)	C13-C14-C15	116(2)
C19-N20-C22	127(2)	C14-C15-C16	121(2)
C29-N30-C32	124(1)	C15-C16-C17	126(2)
C39-N40-C2	123(1)	C16-C17-C18	108(1)
N30-C32-N31	128(1)	C13-C18-C17	120(2)
N30-C32-C33	128(1)	C13-C18-C19	114(2)
N31-C32-C33	105(1)	C17-C18-C19	125(1)
C32-C33-C34	129(1)	N11-C19-C18	100(1)
C32-C33-C38	111(1)	N11-C18-N20	128(2)
C34-C33-C38	121(1)	C18-C19-N20	132(2)
C33-C34-C35	119(1)	N20-C22-N21	130(1)
C34-C35-C36	117(1)	N20-C22-C23	122(1)
C35-C36-C37	128(1)	N21-C22-C23	109(1)
C36-C37-C38	115(1)	C22-C23-C24	136(1)
C33-C38-C37	128(1)	C22-C23-C28	104(1)
C33-C38-C39	104(1)	C23-C28-C29	111(1)
C37-C38-C39	133(1)	C27-C28-C29	130(1)
C38-C39-N31	112(1)	N21-C29-C28	98(1)
N38-C39-N40	121(2)	N21-C29-N30	133(1)
N31-C39-N40	128(2)	C28-C29-N30	128(1)

Phthalocyanine II

N41-Nd-N51	68.9(4)°	N50-C52-N51	131(2)
N41-Nd-N71	69.6(3)	N50-C52-C53	120(2)
N-51-Nd-N61	68.2(4)	N51-C52-C53	110(1)
N61-Nd-N71	69.5(4)	C52-C53-C54	133(1)
Nd-N41-C42	119(1)	C52-C53-C58	107(1)
Nd-N41-C49	120(1)	C53-C58-C59	106(1)
C42-N41-C49	112(1)	C57-C58-C59	134(1)
Nd-N51-C52	119(1)	N51-C59-C58	110(1)
Nd-N51-C59	121(1)	N51-C59-N60	123(1)

C52-N51-C59	108(1)	58-C59-N60	126(1)
Nd-N61-C62	119(2)	N60-C62-N61	124(1)
Nd-N 1-C69	116(1)	N60-C62-C63	124(1)
C62-N61-C69	107(1)	C61-C62-C63	111(1)
Nd-N71-C72	122(1)	C62-C63-C64	134(1)
Nd-N71-C79	123(1)	C62-C63-C68	105(1)
C72-N71-C79	109(1)	C63-C68-C69	106(1)
C49-N50-C52	122(1)	C67-C68-C69	133(1)
C59-N60-C62	125(1)	C61-C69-C68	110(1)
C69-N70-C72	122(1)	C61-C69-N70	132(2)
C79-N80-C42	118(2)	C68-C69-N70	118(2)
N41-C42-C43	104(1)	N70-C72-C71	126(1)
N41-C42-N80	133(2)	N70-C72-C73	126(1)
C43-C42-N80	120(2)	N71-C72-C73	108(1)
C42-C43-C44	133(1)	C72-C73-C74	132(1)
C42-C43-C48	107(1)	C72-C73-C78	108(1)
C43-C48-C49	108(1)	C73-C78-C79	107(1)
C47-C48-C49	132(1)	C77-C78-C79	132(1)
N41-C49-C48	109(1)	N71-C79-C78	108(1)
N41-C49-N50	127(1)	N71-C79-N80	130(1)
C48-C49-N50	124(1)	C78-C79-N80	121(1)

TABLE 5. Deviations of atoms from plane of pthalocyanine macrocycle

Phthalocyanine I		Phthalocyanine II	
Nd -1.70	N21-0.24	Nd 1.60Å	N61 0.07
N1 -0.22	C22-0.13	N41 0.09	C62 0.09
C2 -0.19	C23-0.04	C42-0.11	C63-0.05
C3 -0.18	C24-0.06	C43-0.03	C64-0.04
C4 -0.11	C25-0.11	C44-0.01	C65-0.03
C5 -0.06	C26-0.14	C45-0.00	C66-0.03
C6 -0.07	C27-0.12	C46-0.02	C67-0.05
C7 -0.14	C28-0.07	C47-0.04	C68-0.05
C8 -0.20	C29-0.20	C48-0.05	C69 0.04
C9 -0.07	N30-0.13	C49 0.05	N70 0.05
N10-0.01	N31-0.29	N50 0.05	N71 0.18
N11-0.16	C32-0.15	N51 0.17	C72 0.04
C12 0.07	C33 0.12	C52 0.10	C73-0.04
C13 0.15	C34 0.33	C53 0.02	C74 0.07
C14 0.26	C35 0.65	C54 0.02	C75 0.07
C15 0.27	C36 0.38	C55-0.04	C76-0.03
C16 0.41	C37 0.26	C56-0.10	C77-0.14
C17 0.30	C38 0.06	C57-0.10	C78-0.15
C18 0.22	C39-0.10	C58-0.04	C79-0.04
C19-0.08	N40-0.12	C59-0.11	N80 0.04
N20-0.09	Ave of all atoms of phthalocyanine I -3.30(18)Å	N60-0.06	Ave. of all atoms of phthalocyanine II from phthalocyanine I -3.30(18)Å

Table 6. Comparison of bisphthalocyaninatotin(IV),-uranium(IV), and -neodymium(III).

	Sn(IV)[6]	U(IV)[11]	Nd(III)
Metal-nitrogen, Å	2.34(7)	2.43	2.47(4)
Metal-square nitrogen planes, Å	1.35(2)	1.40	1.47(1)
Rotation of the rings, deg	42	37	45

Table 7. Magnetic Results

	blue Pc_2NdH	green Pc_2NdH
Weiss const. (θ,°K)	-8	40
μ_{eff} (B.M. at 297°K)	3.46(3.62)*	4.24(5.35)**
μ_{eff} (B.M. at 73°K)	3.42	3.65

*The value calculated by putting the values of g = 8/11, J = 4 into an equation of $\mu = \sqrt{J(J+1)g}$.

**Obtained by adding 1.73 (for one organic-free radical) to 3.62.

Figure Captions

Figure 1. Plan view of bisphthalocyaninatoneodymium(III). Upper and down rings are named as segment 1 and segment 2, respectively.

Figure 2. Molecular structure of bisphthalocyaninatoneodymium(III).

Figure 3. X-band EPR signals of the green bisphthalocyaninatoneodymium(III) complex in the solid state at 77°K. The line 2 respects the signal of the green compound diluted by the blue (1:100). Gains are 8.0×10^{1} and 2.0×10^{4} for the line 1 and 2, respectively.

Figure 4. UV light effects on conversion of the blue compound to the green in the tetrahydrofuran solution containing a small amount of dichloromethane. 1) Before irradiation, 2) 2 minutes after irradiation, 3) 4 minutes, 4) 6 minutes, 5) 8 minutes, 6) 10 minutes.

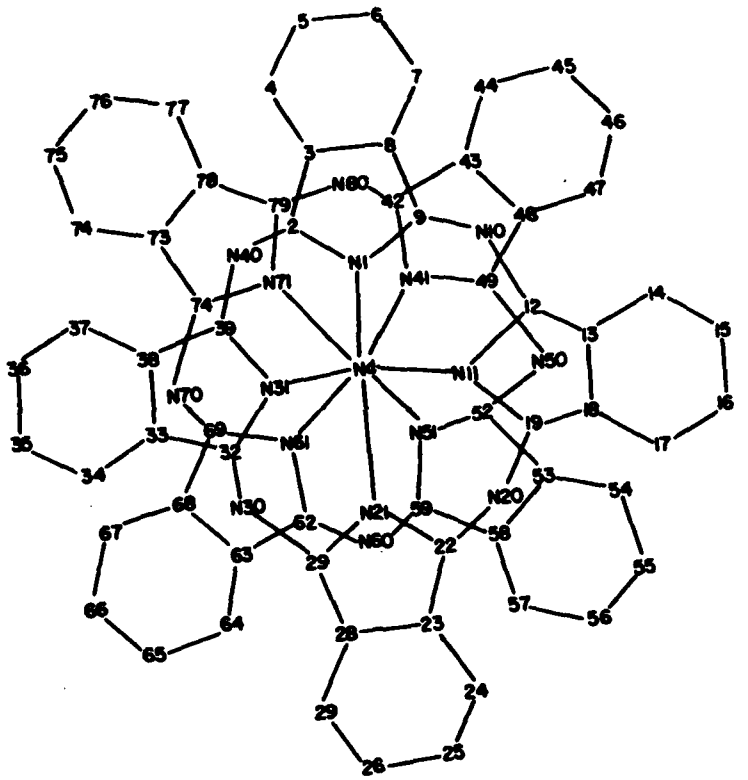
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Figure 1

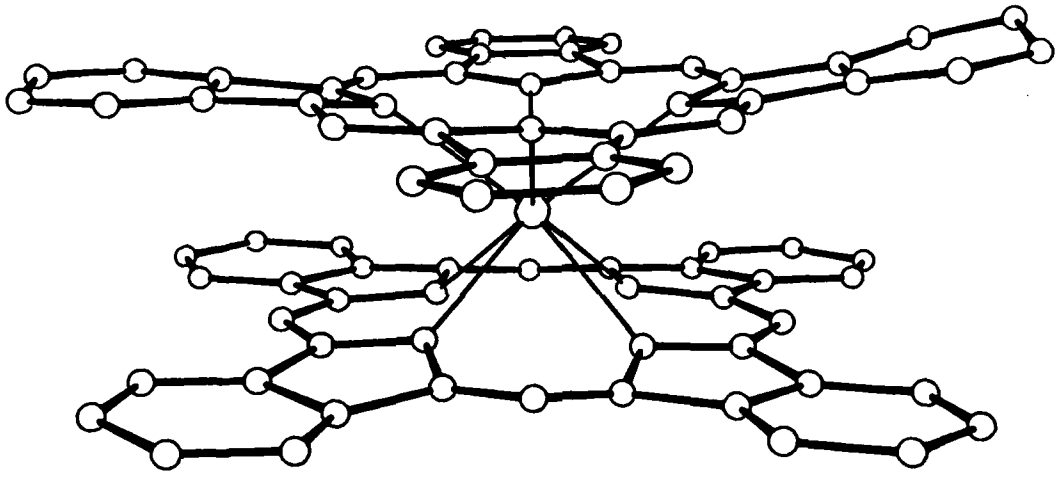


Figure 2

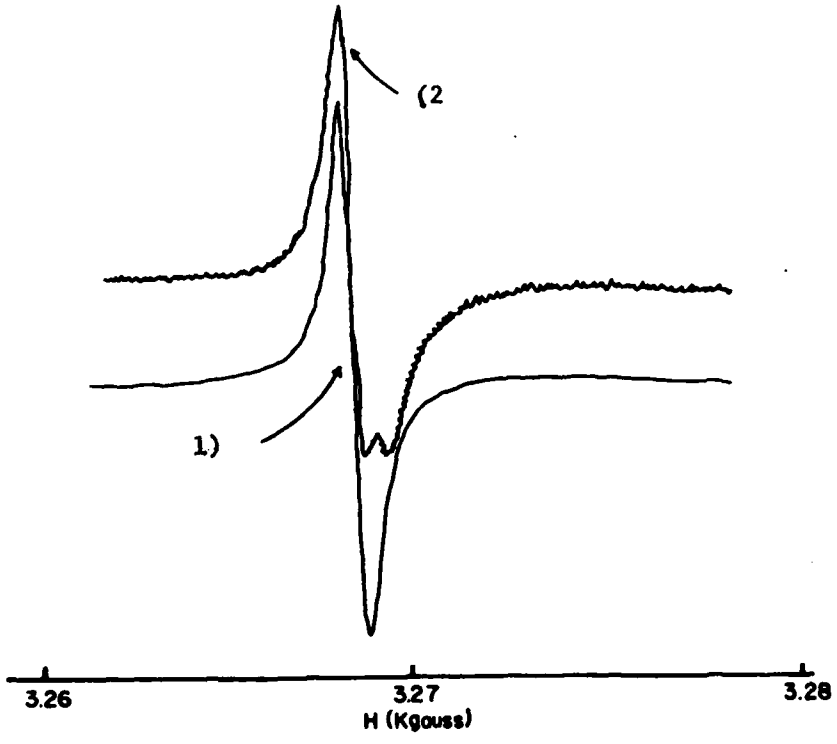


Figure 3

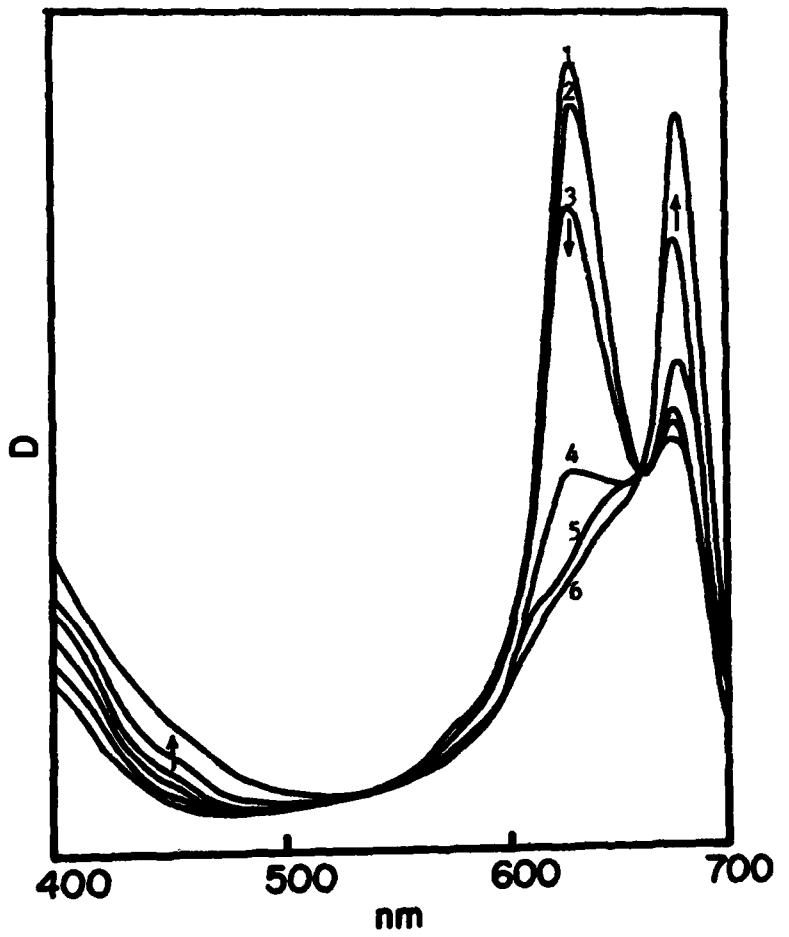
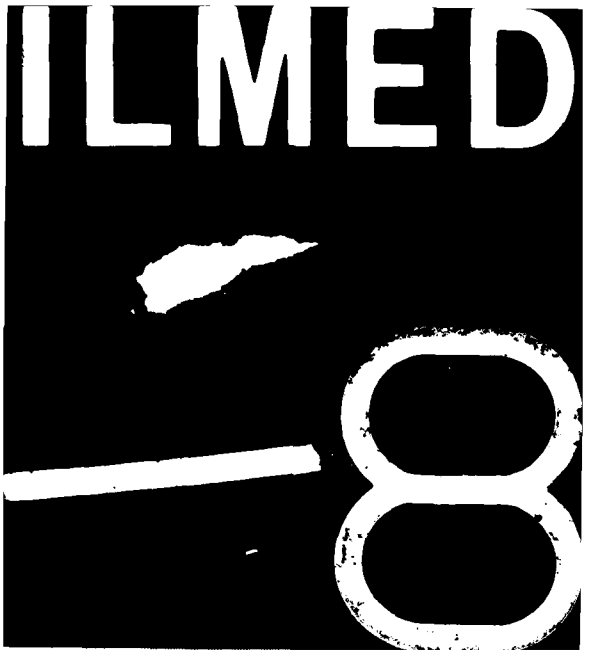


Figure 4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